

## SCIENCE FOR CERAMIC PRODUCTION

*We are bringing to your attention in this and subsequent issues of this journal a series of topical articles by prominent scientists on technical ceramics: V. S. Barkunov — Doctor of Chemical Sciences and Academician of the Russian Academy of Natural Sciences and E. S. Lukin — Doctor of Technical Sciences, Academician of the Russian Academy of Natural Sciences, and Honored Faculty Member of the School of Higher Education of the Russian Federation.*

*The articles are unified by common theme and are of interest for researchers and manufacturers.*

*The articles generalize the results of investigations of ceramic technology based on highly dispersed powders. Analysis of these results shows that the mechanisms of mass transfer during sintering and crystal growth in such objects, obtained by chemical methods, have their own special features as compared with less dispersed particles obtained by mechanical grinding. There is a qualitative difference between the behaviors of these two types of powder due to the structural differences of their constituent particles.*

UDC 666.762-128:666.3.022

### SPECIAL CHARACTERISTICS OF THE TECHNOLOGY OF HIGH-DENSITY TECHNICAL CERAMICS. CHEMICAL METHODS FOR OBTAINING THE INITIAL POWDERS

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Translated from *Steklo i Keramika*, No. 2, pp. 3–7, February, 2008.

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Different methods for fabricating high-dispersity powders of oxides and their compounds are examined. These methods make it possible to obtain dense and strong ceramic materials with a regulatable microstructure. Chemical methods are most commonly used to obtain highly dispersed powders giving a uniform distribution of the components. The method of heterophase precipitation gives hydroxide powders which are x-ray amorphous, filter well, and consist of spherical aggregates 0.5  $\mu\text{m}$  or less in size. On sintering the structure of the hydroxides is transferred to the oxides obtained, from which high-quality ceramic articles are manufactured.

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Conventional oxide ceramics with about 99.9% content of the principal component are characterized by a comparatively low level of the properties and a microstructure which is difficult to regulate. Ordinarily, the density is 95–98%, the bending strength is 100–200 MPa, and the average size of the crystals fluctuates in the range 10–100  $\mu\text{m}$ . At the same time the type of chemical bond and structure of the crystal lattice of refractory oxides impart certain characteristics which other materials do not possess. For example, optically transparent and high-strength articles can be obtained on the basis of oxides – dielectrics [1].

Advances made in the last few years in technology have convincingly shown that the possibilities for producing new types of ceramics have by no means been exhausted. It should be noted that success is linked, first and foremost, with the development of chemical methods for obtaining highly dispersed powders and introducing modifying additives. This made it possible to solve difficult problems of fabricating materials with high and sometimes unique strength, hardness, heat resistance, durability, transparency, and so forth characteristics. It is still difficult to imagine the influence which their application could have on the development of technology. Consequently, many countries have established priority directions for the development of ceramics, adopted national programs, and organized scientific and industrial centers, since only their very unique properties make

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it possible to produce many modern instruments, apparatus, and systems [2].

In [3] the processes involved in ceramic technologies are viewed as accumulation of energy by powder particles at the time the particles are obtained followed by dissipation of this energy in the surface tension force field during sintering of the powdered body formed. We know that sintering presupposes substantial thermal activation of the atoms (ions) to accelerate mass transfer, since solids have a very high viscosity. The production of dispersed particles is also activation, since energy accumulation by the particles occurs. This is due to an increase of the surface energy as a result of an increase in the size and curvature of the surface. The volume energy of the particles also increases as result of the formation of local stressed sites and defects in the crystal lattice.

The present article presents the results of the study of the behavior of highly dispersed powders, obtained by chemical methods, and considerations concerning the physical – chemical processes occurring in the technology of ceramics based on such powders.

The direction “technical ceramics” is being developed within the framework of ceramics technology. The main purpose of this direction is to develop methods to obtain materials with prescribed specific properties (construction, electrically conducting, transparent, heat conducting, heat resistant, luminescent, highly conducting, and so forth ceramics). In the process, a more profound and deeper understanding of the connections and mechanisms forming the basis of the formula “dispersity – composition – structure – property” has been gained [1]. In this case, sintering is substantially accelerated and even the mechanism of pore removal is different. The coefficient of diffusion increases appreciably when additives, forming solid solutions with the appearance of point defects, are introduced; the concentration of defects responsible for mass transfer can be regulated by the quantity of additives. In summary, the flow of the densification process can be greatly influenced by purposefully changing the characteristics of the powders.

Ways to obtain powders which are active with respect to sintering were known previously. The concept “activity” still remains unclear; different authors often interpret it differently. Ordinarily, activity is associated with the presence of distortions of the type dislocations, crystal boundaries, microscopic disruptions of continuity, and so forth arising in the crystal lattice during grinding [4, 5]. It is assumed that the temperature stability of bond distortions, displacements of atoms from their regular positions, and microstresses localized within a single element of the substructure is inadequate. Indeed, the existing experimental data show that such stresses relax during heating up to low temperatures. In this connection, different authors propose their own suggestions concerning the nature of activity. For example, V. A. Ivensen advance a hypothesis based on the relation of crystal flow with short-lived active imperfections formed as a result of the annihilation of the initial defects; other points of view also exist [6].

A characteristic feature of chemical methods for obtaining powders is that they are conducted far from equilibrium [7]. As a result, new growth actually stops at the crystal nucleation stage: nanometer-size particles which are highly dispersed and very defective and possess a highly extended surface (interior and exterior) arise. Their shape is approximately round, and the crystal structure is strongly distorted — right up to x-ray amorphous.

All this can be regarded as the creation of a system of accumulating structures during mechanical grinding and in chemical methods of production. In other words, this is activation of particles — chemical or mechanical. In the text below, “activity” is associated with the dispersity of the particles, since methods exist for determining their size quantitatively (microscopy, garment of surface area), while stresses, distortions, and so forth in the overwhelming majority of the cases can only be judged qualitatively.

## CHEMICAL METHODS FOR PRODUCING THE INITIAL POWDERS

The simplest and most widely used in ceramic technology (including in industry) method for obtaining articles with multiple components in their composition is based on mixing and simultaneously pulverizing oxide powders, synthesis of new growths in a solid phase, and sintering the growths. The character and intensity of the interaction between the initial components strongly depend on the dispersity of the powders and the uniformity of their mixing. However, when the oxide method is used it is very difficult to attain uniformity of the distribution of small quantities of the additive even with prolonged combined milling, since the additive particles must be dispersed to much smaller sizes than the particles of the main oxide. Otherwise, when particles have comparable sizes local composition nonuniformities appear, resulting in nonuniformity of the microstructure and a large variance of the properties of the articles. Consequently, commercially manufactured oxides often do not make it possible to obtain materials with the required quality. Nonetheless, the method is used to make, for example, ferrites stabilized by  $\text{ZrO}_2$  and so forth, but there are difficulties in obtaining reproducible microstructure and properties. In the number of cases, it gives quite stable results, a specific example being the production of transparent articles based on  $\text{Y}_2\text{O}_3$  with the addition of  $\text{ZrO}_2$ , as well as high-strength ceramics in the system  $\text{Al}_2\text{O}_3 - \text{ZrO}_2$ .

To increase the uniformity of the distribution of the components, the initial pastes are obtained through intermediate compounds. For example, often the main material is in the form of oxide and the additive is in the form of a salt solution. This requires prolonged wet grinding and subsequent drying or treatment with an ammonia solution, heating the batch for synthesizing oxides (or solid solutions), and additional grinding of the product. The method makes it possible to obtain, for example, a quite transparent ceramic from

$Y_2O_3$  and alumina-magnesia spinel. However, light transmission of the materials obtained does not reach its maximum value [8, 9].

Uniform mixing of the components is achieved by using a mixture of crystal hydrates of the corresponding salts. In the process of heating, the mixture first melts, forming a solution in its own crystallization water. Then, when the water is removed from it a solid solution of the salts is separated. Next, it is heated above the decomposition temperature to synthesize a solid solution of oxides. The powder obtained, as a rule, is aggregated and requires milling to particle size less than  $2\text{ }\mu\text{m}$ . The method has been used to obtain transparent ceramic from yttrium oxide and alumina-magnesia spinel, but it is not widely used because of a number of drawbacks: it is inefficient, aggressive gases are released, the uniformity of the chemical composition can be destroyed, and the powders are characterized by strong aggregation of the particles [10].

In certain cases, the technological solution is to use other methods, for example, combined grinding followed by heating of mixtures of insoluble compounds, such as oxalates, carbonates, and hydroxides of the corresponding elements. The method is quite effective, but the problem of obtaining compositions with a uniform distribution of the components is not always solved.

The most common and promising methods for obtaining products with high homogeneity and complex composition are relatively low-temperature methods for preparing powders of oxide materials under strongly nonequilibrium conditions. These include combined precipitation of reagents, spray drying, cryochemical crystallization, the sol – gel process, and heterophase chemical interaction [9, 11].

Methods which yield solid solutions of salts (oxalates, carbonates) or hydroxides, specifically, their co-precipitation from solutions of easily soluble salts of the components, are especially effective. The uniformity of the precipitates crystallizing during mixing with precipitating agents is determined by their mutual solubility in the solid-state and the crystallization rate of the components. The large difference in the precipitation rates of individual substances makes it difficult to obtain uniform crystals, but there are ways to perfect this method [12].

Precipitation of concentrated salt solutions with temperature  $90 - 100^\circ\text{C}$  and separation of the mother liquor by filtration holds great possibilities for obtaining x-ray amorphous precipitates with a uniform distribution of the components. Creating a high degree of supersaturation makes it possible to obtain high homogeneity of the components and high dispersity of the primary particles when using a solution of the precipitating agent cooled below room temperature. The precipitated compounds consist of  $50 - 100\text{ }\mu\text{m}$  aggregates, themselves consisting of particles with size  $2\text{ }\mu\text{m}$  and smaller. They filter well, and their de-aggregation makes it possible to obtain, after heating, highly dispersed and disaggregated powders of solid solutions or compounds of

oxides. In most cases such powders can be used to make articles without additional grinding. This method has been used to obtain high-quality ceramic materials based on yttrium scandate, optically transparent materials based on  $Y_2O_3$  and  $Sc_2O_3$ , and yttrium – aluminum garnet [11].

One way to improve the co-precipitation method is to disperse mixtures of hot concentrated solutions of salts and a solution of the precipitating agent (reverse order of precipitation). This sharply decreases their interaction time and gives a highly uniform distribution of the components in highly dispersed (less than  $1\text{ }\mu\text{m}$ ) particles of the precipitated compounds. At the same time, the technological properties of the powders improve, specifically, their filtration coefficient increases by three to four orders of magnitude compared with the filtration coefficient of powders obtained from dilute solutions.

Experience shows that the properties of the powders are identical irrespective of the conditions of dispersion of the salt solution. Apparently, the particles crystallize at the moment of impact of the solution of the precipitating agent against a surface with a very rapid chemical interaction [11].

The method of solvent replacement is based on the “salting out” effect — a sharp decrease of the solubility of the salts in water – organic mixtures compared with the solubility in pure water. It has a number of drawbacks so that it is rarely used to obtain solid solutions of salts: a quite a large amount of organic solvents must be used, aggressive gases are released during heating of the intermediate salts, salts are differentiated, and so forth.

Spray drying consists in dispersing the initial solution in a coolant stream and dehydration; in most cases the coolant is heated air. The method has been used successfully to obtain manganese – zinc ferrites from sulfate solutions at relatively low temperatures in the melting zone ( $280 - 300^\circ\text{C}$ ). The drawback of this method is the cumbersomeness of the special equipment used.

The cryochemical method is based on dispersing the initial solutions of salts of oxide-forming components in a liquid cooling agent which does not mix with the precipitating agent. “Instantaneous” freezing makes it possible to obtain a cryochemical product — spherical ice granules with the initial salt components distributed uniformly over the volume of the granules. The method makes it possible to distribute components uniformly, but it has a number of drawbacks which greatly limit its application, first and foremost, special equipment is required and the technological process is time-consuming.

The method of heterophase synthesis consists in obtaining a crystal-like, low-hydrated, insoluble hydroxy compound by a chemical interaction of a solid soluble salt of the main component with a base (for example,  $NH_4OH$ ) or acid (for example,  $H_2CO_3$ ) solution. It has been determined that obtaining some solid compounds from others initially results in the formation of disordered amorphous phases of hydroxy compounds. These compounds contain virtually no absorbed

TABLE 1.

Material*	Hydroxides		Oxides		Ceramic			
	specific surface area, m <sup>2</sup> /g	filtration coefficient, cm/sec	crystallization temperature, °C	specific surface area, m <sup>2</sup> /g	firing temperature, °C	relative density, %	predominant crystal size, 1 μm	bending strength, MPa
Y <sub>2</sub> O <sub>3</sub>	75	80	720	35	1700	99.5	30 – 40	120 ± 20
Sc <sub>2</sub> O <sub>3</sub>	85	50	750	30	1700	99.5	10 – 15	150 ± 20
Al <sub>2</sub> O <sub>3</sub> – MgO	80	50	1350	4	1550	99.9	5 – 10	350 ± 40
3Y <sub>2</sub> O <sub>3</sub> · 5Al <sub>2</sub> O <sub>3</sub>	110	70	780	25	1750	99.8	15 – 20	190 ± 30
Y <sub>2</sub> O <sub>3</sub> – HfO <sub>2</sub>	90	50	780	35	1750	100.0	10 – 15	150 ± 30
Y <sub>2</sub> O <sub>3</sub> – Sc <sub>2</sub> O <sub>3</sub> – HfO <sub>2</sub>	80	30	790	30	1750	100.0	5 – 8	300 ± 40
Sc <sub>2</sub> O <sub>3</sub> – La <sub>2</sub> O <sub>3</sub>	90	60	950	15	1650	99.9	8 – 10	280 ± 30
3Y <sub>2</sub> O <sub>3</sub> · 5Al <sub>2</sub> O <sub>3</sub> · Sc <sub>2</sub> O <sub>3</sub>	105	40	820	20	1750	100.0	25 – 30	290 ± 25
Al <sub>2</sub> O <sub>3</sub> – ZrO <sub>2</sub> – Y <sub>2</sub> O <sub>3</sub>	120	50	1350	3	1720	99.9	1 – 3	800 ± 50
Al <sub>2</sub> O <sub>3</sub> – Sc <sub>2</sub> O <sub>3</sub> – MgO	85	70	1350	5	1550	99.9	2 – 5	700 ± 50
Al <sub>2</sub> O <sub>3</sub> – TiO <sub>2</sub> – Sc <sub>2</sub> O <sub>3</sub>	100	80	1300	5	1650	98.5	5	100 ± 10
ZrO <sub>2</sub> – Y <sub>2</sub> O <sub>3</sub>	95	50	480	45	1500	99.9	0.5 – 0.8	750 ± 50

\* The aggregates of oxide and hydroxide powders are less than 1 μm in size.

water or undesirable anions and they consist of a product with little water. Characteristically, a polymer structure with Me – O as the main bond is formed. A special feature of this method is that when the solid salt is converted into an insoluble compound the framework of the initial structure is inherited. The particles obtained have sharp boundaries, and their surface in solution and in air is preserved for a long time without any visible changes, i.e., no tendency toward aggregation is observed. Then powders are easily filtered and settle well after agitation, which is where their crystal-like character is expressed. At the same time, they are x-ray amorphous because the primary crystals are very small [13, 14].

The interaction occurs not only on the surface of the particles but also in their volume, so that the distribution of the substances introduced is quite uniform.

A modification of the method was used to increase the dispersity of the initial solid particles of salts in order to transfer them by a heterophase interaction into an insoluble compound, specifically, dispersing by a dispersing a saturated solution of salts at 100 – 110°C in a solution of a precipitating agent. Drops in flight cool to the crystallization temperature, which makes it possible to preserve completely the distribution of the components at the molecular level; entering the precipitating agent, they are converted into insoluble compounds almost immediately. Since the particles are very small size (less than 1 μm in size), the formation of strong intramolecular bonds characteristic for oxides occurs very quickly. We note that precipitates of insoluble compounds of different elements precipitated in this manner have little water and are crystal-like, and the particles formed are nearly spherical. The absence of reflections in x-ray diffraction patterns of freshly prepared products attests to their

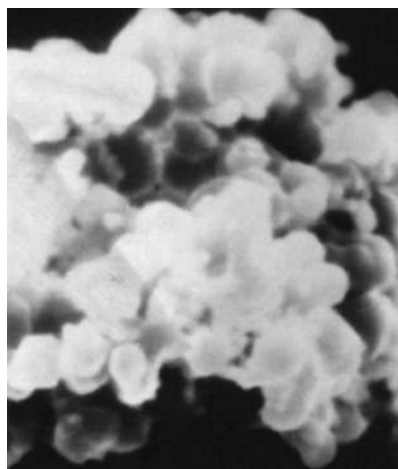
x-ray amorphousness. At the same time, they behave similarly to crystals, since there is no aggregation of particles during precipitation and subsequent filtering and drying. This is due mainly to the low water content of the precipitates. In all cases, only one endothermal effect was observed during decomposition of the products. This effect attests to the formation of solid solutions of hydroxides.

To obtain particles of precipitated compounds with size equal to a fraction of a micron, before heating they must be subjected to brief disaggregation by the wet method (for example, in water, acetone, alcohol, and so forth). When the intermediate products are heated, their structure is transferred to the oxides. The particles whose size falls in the range 0.2 – 0.5 μm are either dense aggregates or individual particles; their shape is rounded or slightly faceted.

The method developed has been used to obtain powders of individual oxides, compounds, solid solutions, and multiphase systems. The presence of corresponding phases is confirmed by optical microscopy and x-ray phase analysis. Ceramic samples have been prepared from the powders, and the microstructure and basic properties of the ceramics have been studied. Some characteristics of the ceramics are presented in Table 1 [11].

The method developed has made it possible to solve the important problem of obtaining powders of intermediate insoluble compounds with aggregates less than 1 μm in size (average size 0.5 μm) and spherical particles. This is achieved by dispersing heated, maximally concentrated, solutions of salts in concentrated ammonia. During heating at definite temperatures, hydroxides convert into highly dispersed powders of oxides or compounds, inheriting the structure and sizes of the aggregates of the precipitated powders.





**Fig. 1.** Particles of oxide powder obtained by dispersing solutions ( $\times 10,000$ ).

The oxide powders obtained in this manner retain their structure for a long period of time (longer than 3 months). This method has also made it possible to obtain a uniform distribution of components over the volume of the particles, which is a necessary condition for maximizing the effect of additives. The most uniform distribution of phases is obtained in multiphase ceramics, giving high values for the properties (for example, the high-strength ceramic based on  $\text{Al}_2\text{O}_3 - \text{ZrO}_2$ , alkali-resistant construction material in the system  $\text{Sc}_2\text{O}_3 - \text{La}_2\text{O}_3$ ) [11].

The general structural features of powders, the technology of samples and articles, and the mechanisms of the sintering of the materials investigated consist of the following. The powders are characterized by approximately the same size of the aggregates (fractions of a micron), spherical shape (see Fig. 1), and a uniform distribution of the components.

The methods used to form samples and articles from them can be different: semidry pressing, hot casting of paraffined slips, water casting in gypsum molds, hydrostatic pressing, and others. A special structural feature of blanks is their uniform finely dispersed structure allowing for uniform sintering during firing. Their relative density is 45 – 60% of the theoretical density depending on the method used. The densification onset temperature in all cases is approximately 200 – 300°C lower than for samples fabricated from commercial powders.

The sintering temperature also decreases, very substantially in some materials. For example,  $\text{Y}_2\text{O}_3$  and  $\text{Sc}_2\text{O}_3$  sinter at 1700°C to density 97% of the theoretical value. Scandium oxide with lanthanum oxide added sinters to density 99.5% of the theoretical value at 1650°C. At the same time, powders precipitated from concentrated solutions without dispersion must be heated up to 1900°C. Samples without  $\text{Al}_2\text{O}_3$  and with the addition of 0.25 wt.% MgO sinter to the theoret-

ical density in vacuum at 1550°C. Materials in the systems  $\text{Y}_2\text{O}_3 - \text{Sc}_2\text{O}_3 - \text{HfO}_2$  and  $\text{Al}_2\text{O}_3 - \text{ZrO}_2 - \text{Y}_2\text{O}_3$  sinter at 1600 – 1700°C to the theoretical density. When commercial oxide powders are used, the materials do not sinter completely at 1700°C and their open porosity is 5 – 8%. Highly dispersed powders permits articles from partially stabilized  $\text{ZrO}_2$  to be sintered at 1450 – 1600 °C to the theoretical density; the bending strength of the articles reaches 800 MPa.

The linear shrinkage of these samples and articles depends on the heating temperature when obtaining oxides and the formation method. It equals 15 – 25%.

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